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(19)

(54) APPARATUS FOR AND PROCESS OF METAL COATING

(71) I, SECRETARY OF STATE FOR DEFENCE, LONDON, do hereby declare the invention for which I pray a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:

The present invention is concerned with apparatus suitable for the deposition of metal upon metal articles and with processes carried out in such apparatus.

In many instances it is necessary to provide a metal coating on a part. This may be for ornamental purposes or, more frequently it is necessary to provide a protective coating on a part to protect it against an adverse environment. For example steel may be protected against corrosion by being coated with cadmium. It may also be possible to deposit a metal in such a thickness that it is capable of removal from the substrate and of being subjected to metallurgical working.

Coating may be by means of an electrolytic technique, an electroless technique or by deposition from the vapour phase. In all techniques cleanliness of the substrate is most important and in vacuum deposition techniques although the metal substrate is subjected to conventional cleaning techniques, eg solvent cleaning, cleaning may be completed once the metal substrate is in position in the vacuum deposition apparatus by means of a glow discharge, frequently an argon glow discharge. See for example UK Patent Specification No 1,109,316 which is concerned with the coating of steel with cadmium for corrosion protection.

Deposition apparatuses are known which include within a vacuum or low pressure system a source of coating material, means to prevent the material impinging the substrate except when desired, a low pressure capable of sustaining a glow discharge, means by which the substrate may in operation be made the cathode of a glow discharge so that positive ions generated in the glow discharge impinge upon the substrate as cathode and exert a cleaning influence thereon. The source of material to be deposited may be a heated evaporative source, a sputtering source or an appropriate crackable gas, for example nickel carbonyl may be a source of nickel. Advantageously the deposited material is a metal. Conventionally argon gas is provided to the apparatus so that an argon glow discharge takes place.

We have discovered that the cleaning action associated with this type of glow discharge, which is called a cold cathode discharge because the cathode is unheated (apart from heating caused by ion impact), cannot be effectively maintained if the substrate temperature exceeds about 300°C. The efficient cleaning of hot substrates by this method is thus impossible. Furthermore the relatively high pressure of about 4×10^{-2} torr required to sustain a cold cathode discharge in argon causes undesirable scattering of the beam of evaporated metal by residual gas in the low pressure system and also precludes the use of the conventional type of hot filament electron gun for heating the evaporation source.

In accordance with the present invention a vacuum deposition apparatus includes, within a vacuum or low pressure system, a source of coating material, which is molten metal; a substrate upon which the material is to be deposited; means to prevent the material impinging upon the substrate except when desired; an electron source and an anode and means to produce in operation a glow discharge between the electron source and the anode arranged so that the substrate is within the glow discharge; means to control the electrical potential of the substrate, electron source and anode relative to one another so that the substrate

is at a negative potential and positive ions produced in the glow discharge impinge upon the substrate and exert a cleaning action thereon; and electromagnetic means arranged to be capable of concentrating the glow discharge around the substrate.

In a preferred embodiment the electron source is a filament electron source. Preferably an argon glow discharge is employed.

The electromagnetic means is preferably at least one circumferentially wound coil within the vacuum or low pressure system arranged so that the metal substrate lies substantially at the axis of the coil. If two coils are employed the coils are substantially parallel and the metal substrate lies at their common axis and substantially at the mid-point between them.

In accordance with an important feature of the present invention in an apparatus of the type set forth above for the deposition of metal upon a metal substrate from the vapour phase the means to control the electrical potential of the metal substrate, electron source and anode relative to one another is also capable of maintaining the electrical potential of the substrate positive with respect to the electron source so that electrons present in the glow discharge impinge upon the substrate and exert a heating action thereon.

In accordance with a particular aspect of the present invention apparatus suitable for the deposition of a metal from the vapour phase upon a metal substrate includes a vacuum or low pressure chamber capable of pressure control in the region 10^{-3} to 10^{-5} torr containing the metal substrate, a heated source means from which in operation the metal is evaporated from the melt arranged so that the metal evaporated impinges upon the metal substrate, the heated source means being provided with a removable shutter, a means by which argon may be introduced into the vacuum chamber, a filament electron source and an anode and means to produce an argon glow discharge between the filament electron source and the anode arranged so that the metal substrate is within the argon glow discharge, means to control the electrical potential of the metal substrate, filament electron source and anode relative to one another so that the metal substrate is maintained at a negative potential and positive argon ions produced in the glow discharge will impinge upon the metal substrate and exert a cleaning action thereon, and electromagnetic means arranged to be capable in operation of concentrating the argon glow discharge around the metal substrate.

In order to ensure good adhesion of the metal deposit to the metal substrate and also to ensure that the desired metallurgical structure is obtained in the deposited metal it may be necessary to control the temperature of the metal substrate and in particular it may be necessary to control the temperature of the metal substrate at a relatively high temperature during the deposition. For example if the metal substrate is a superalloy such as is normally used in turbine blades the metal substrate temperature is preferably controlled within the range 300 to 1200°C and normally towards the upper portion of that range.

In apparatus of the present invention the metal substrate may be heated by ion bombardment or by electron bombardment either using the filament electron source of the glow discharge, that is in accordance with the aforementioned feature of the present invention or by using an additional electron source. Preferably the filament electron source of the glow discharge is used as the electron source for heating the metal substrate and in order to carry this out the filament electron source is maintained at a negative potential relative to the metal substrate. In this way heating of the metal substrate is carried out by use of the aforementioned important feature of the present invention and it is contemplated that the metal substrate may be heated but not necessarily cleaned by a glow discharge method.

When the principal means of heating is electron bombardment heating then means are provided so that the apparatus can switch from the heating to the cleaning mode and it has been found advantageous to switch at a frequency of about one or two times per minute although shorter or longer periods can be used.

The metal substrate may be stationary but preferably it is arranged to move relative to the heated source means in order to ensure even deposition. If the metal substrate is an article, such as a turbine blade, which must be uniformly coated it is preferably rotated so that the metal is deposited evenly.

Preferably the heated source means from which the metal is evaporated is heated by electron beam heating and an ingot is fed into a cooled crucible at such a speed that the feed rate of the crucible equals the rate of removal of metal by evaporation. Advantageously the crucible comprises a cooled annular crucible and the ingot is fed into the bottom of the crucible while the electron beam impinges upon the upper surface of the ingot.

Alloys may be evaporated in like manner to pure metals by such a heated source means. After a certain time a steady state is reached and the composition of the metal deposited on the substrate is constant. For this reason a shutter is necessary to prevent

the metal evaporated before the steady state is reached impinging on the metal substrate. The composition of the pool of molten feed metal may not be the same as either the feed ingot or the deposited material, its sole purpose is to provide a reservoir from which material of the appropriate composition evaporates.

Typical electron beam heating apparatus operates at a pressure below about 5×10^{-4} torr and preferred deposition apparatus of this invention is adapted to operate in this region.

Advantageously the electron beam heating apparatus includes an electron gun or guns in which the electron beam is turned through 270° so that the opening of the gun is not pointed upwards and therefore open to receive stray pieces of metal and the like falling from the upper parts of the apparatus. This arrangement has the further advantage that the magnets and the electron gun may be below the level of the crucible of evaporating metal so that the magnets of the electron beam heating apparatus are not coated by evaporating metal.

The cleaning action of the glow discharge as described is effective at the pressure at which the electron beam heating apparatus operates, nominally about 5×10^{-4} torr and below, and a preferred deposition apparatus of this invention is arranged for pressure control in this region.

Ideally to ensure the best possible adhesion of the deposited metal to the metal substrate cleaning should be carried out until the initial stage of deposition but it has been discovered that if the metal substrate is at a temperature below about 300°C the argon ions which clean the substrate surface are themselves trapped by the deposited metal and on subsequent heating can form bubbles which cause cracks and other faults in the deposit. Accordingly apparatus of the present invention is arranged to that cleaning may be stopped at least as soon as deposition starts, or the metal substrate may be heated to higher temperature during deposition.

The apparatus disclosed hereinbefore may be used in processes for depositing metal from the vapour phase upon a metal substrate and in accordance with a further aspect of the present invention a process for the deposition of metal from the vapour phase upon a metal substrate includes the step of cleaning the metal substrate by placing the metal substrate in an argon glow discharge between a filament electron source and an anode, concentrating the argon glow discharge around the metal substrate by magnetic means and maintaining the metal substrate at a negative potential so that positive argon ions generated in the glow discharge impinge upon the metal substrate and exert a cleaning action thereon.

Apparatus, and its mode of operation, in accordance with the present invention will now be described by way of example only and with reference to the schematic cross-sectional drawing accompanying the Provisional Specification.

The apparatus comprises a vacuum vessel 10 which is evacuated by a conventional vacuum pump 11. The pressure within the vacuum vessel 10 is monitored by the pressure gauge 12 and the vacuum vessel is provided with an argon supply 13 through a needle valve 14. Within the vacuum vessel 10 a metal substrate 15 is rotatably mounted upon a shaft 16 which passes through a seal 17 in the wall of the vacuum vessel 10 and is driven by an electric motor 18. Below the metal substrate 15 is disposed an evaporative source means 19 which comprises a water cooled annular copper crucible 20 having inlet and outlet water coolant pipes 21 passing through a seal 22 in the wall of the vacuum vessel 10. An ingot 23 is fed upwards through the crucible 20 by a feed mechanism 24, the electrical leads 25 to which pass through a seal 26 in the wall of the vacuum vessel 10. Electrons from an electron gun 27, supplied with electrical power by electrical leads 28 through a seal 29 in the wall of the vacuum vessel 10, are focussed by means of a magnet 30 to follow a path within the envelope 31 and impinge upon the top of the ingot 23 to form a pool 32 of molten metal contained by the solid metal of the ingot 23 and the water cooled crucible 20. A removable shutter 33, operable by a handle 34, through a seal 35 in the wall of the vessel 10, is interposed between the heated source means 19 and the metal substrate 15. A filament electron source 36 and an anode 37 are disposed on opposite sides of the substrate 15 and means 38, not shown in detail, are provided by which the relative electrical potentials of the electron filament source 36, the substrate 15 and the anode 37 can be controlled relative to one another. Leads from this control means 38 pass through a seal 39 in wall of the vacuum vessel 10. Two of the possible modes of operation available are: (1) ion-bombardment cleaning of the substrate 15 in which the argon pressure is 5×10^{-4} torr and the substrate 15 is maintained at −500 volts and the anode 37 at +80 volts both with respect to electron filament source 36 at 0 volts, and (2) electron bombardment heating of the substrate 15 in which the argon pressure is 1.5×10^{-3} torr and the substrate is held at +300 volts with respect to the electron filament source 36 at 0 volts and the anode 37 voltage is allowed to float.

An upper coil 40 and a lower coil 41, both circumferentially wound, are provided, and supplied with electrical power through leads 42 passing through a seal 43 in the wall of the vacuum vessel 10. These coils 40 and 41 are arranged in operation to concentrate the cleaning or heating argon glow discharge between the electron filament 36 and the substrate 15 and/or the anode 37 in the region of the substrate 15.

In operation the metal ingot 23 is heated to the evaporation temperature by means of the electron gun 27 with the shutter 33 in position. This is to allow the composition of the vapour to reach equilibrium. At the same time the substrate is subjected to ion bombardment cleaning and is spun by means of the electric motor 17. Ion bombardment cleaning provides a certain heating effect, but if the substrate 15 is to be at a high temperature the control 38 is adjusted to provide electron bombardment heating. The control 38 can be adjusted to provide alternate periods of cleaning and heating of appropriate length. Preferably the total cleaning period is as short as is compatible with adequate cleaning. Once equilibrium has been reached and the vapour evaporating has constant composition, the shutter 33 is removed by means of the handle 34 and the metal evaporating from the source means 19 allowed to impinge upon the substrate 15. The cleaning effect of the argon glow discharge is stopped simultaneously with or immediately before the opening of the shutter because of the deleterious effect of argon bubbles which may be formed if cleaning and deposition are carried on simultaneously.

The deposition is carried on until the appropriate thickness of deposit has been made and is then stopped by closing the shutter 33. The substrate may then be removed from the vacuum vessel 10.

The substrate 15 may be heated by means of electron bombardment heating during deposition, in order to maintain the temperature of the substrate 15 at a desired level or after the deposition is ended, in order to heat treat the deposited layer, as well as before deposition starts.

In the accompanying schematic drawing the electron filament source 36 is shown in line with the source means 20 and the substrate 15. In an alternative arrangement the electron filament source 36 may be arranged in a plane substantially perpendicular to the line through the source means 20 and the substrate 15, with the anode 37 in the same plane but disposed on the side of substrate 15 remote from the electron filament source 36. The coils 40 and 41 in this instance are also arranged at right angles to the portion illustrated in the accompanying drawing so that they can concentrate the argon glow discharge between the electron filament 36 and the substrate 15 and/or the anode 37 in the region of the substrate 15.

WHAT I CLAIM IS:

1. A vacuum deposition apparatus which includes, within a vacuum or low pressure system, a source of coating material, which is molten metal; a substrate upon which the material is to be deposited; means to prevent the material impinging upon the substrate except when desired; an electron source and an anode and means to produce in operation a glow discharge between the electron source and the anode arranged so that the substrate is within the glow discharge; means to control the electrical potential of the substrate, electron source and anode relative to one another so that the substrate is at a negative potential and positive ions produced in the glow discharge impinge upon the substrate and exert a cleaning action thereon; and electromagnetic means arranged to be capable of concentrating the glow discharge around the substrate.

2. Apparatus as claimed in claim 1 and wherein the electron source is a filament electron source.

3. Apparatus as claimed in claim 1 or claim 2 and wherein the glow discharge is an argon glow discharge.

4. Apparatus suitable for the deposition of metal from the vapour phase upon a metal substrate which includes a vacuum or low pressure chamber capable of pressure control in the region 10^{-3} to 10^{-5} torr containing the metal substrate, a heated source means from which in operation the metal is evaporated from the melt arranged so that the metal evaporated impinges upon the metal substrate, the heated source means being provided with a removable shutter, a means by which argon may be introduced into the vacuum chamber, a filament electron source and an anode and means to produce an argon glow discharge between the filament electron source and the anode arranged so that the metal substrate is within the argon glow discharge, means to control the electrical potential of the metal substrate, filament electron source and anode relative to one another so that the metal substrate is at a negative potential and positive argon ions produced in the glow discharge impinge upon the metal substrate and exert a cleaning action thereon, and electromagnetic means arranged to be capable in operation of concentrating the argon glow discharge around the metal substrate.

5. Apparatus as claimed in any one preceding claim and wherein the electromagnetic means consists of at least one circumferentially wound coil within the

vacuum or low pressure system arranged so that the metal substrate lies substantially at the axis of the coil.

6. Apparatus as claimed in any preceding claim wherein the substrate is provided with means to maintain its temperature within the range 300 to 1200°C.

7. Apparatus as claimed in claim 6 wherein the substrate is metal and heating of the metal substrate is by electron bombardment and means are provided to maintain the electron source at a negative potential relative to the metal substrate.

8. Apparatus as claimed in claim 7 wherein means are provided so that the metal substrate is either at a positive potential relative to the electron source or at a negative potential relative to the electron source and is capable of being switched between these two states.

9. Apparatus as claimed in any one preceding claim wherein the metal substrate is capable of movement relative to the heated source means to ensure even deposition of metal.

10. Apparatus as claimed in any one preceding claim wherein the heated source means from which the metal is evaporated is heated by electron beam heating and an ingot is fed into a cooled crucible at such a speed that the feed rate of the metal into the crucible equals the rate of removal of metal by evaporation.

11. Apparatus as claimed in claim 10 wherein the crucible comprises a cooled annular crucible and the ingot is fed into the bottom of the crucible while the electron beam impinges upon the upper surface of the ingot.

12. A process for the deposition of metal from the vapour phase upon a metal substrate which includes the step of cleaning the metal substrate by placing the metal substrate in an argon glow discharge between a filament electron source and an anode, concentrating the argon glow discharge around the metal substrate by electromagnetic means and maintaining the metal substrate at a negative potential so that positive argon ions generated in the glow discharge impinge upon the metal substrate and exert a cleaning action thereon.

13. Apparatus substantially as hereinbefore disclosed and with particular reference to the drawing accompanying the Provisional Specification.

14. A vacuum deposition apparatus which includes, within a vacuum or low pressure system, a source of coating material, which is molten metal; a substrate upon which the material is to be deposited; means to prevent the material impinging upon the substrate except when desired; an electron source and an anode and means to produce in operation a glow discharge between the electron source and the anode arranged so that the substrate is within the glow discharge; means to control the electrical potential of the metal substrate positive with respect to the electron source such that electrons present in the glow discharge impinge upon the substrate and exert a heating action thereon, and electromagnetic means arranged to be capable in operation of concentrating the glow discharge around the substrate.

15. Apparatus as claimed in claim 14 and wherein the electron source is a filament electron source.

16. Apparatus as claimed in claim 14 or claim 15 and wherein the electromagnetic means consists of at least one circumferentially wound coil within the vacuum or low pressure system so that the metal substrate lies substantially at the axis of the coil.

17. Apparatus suitable for the deposition of metal from the vapour phase and wherein the method of heating the metal substrate is by glow discharge substantially as hereinbefore described and with particular reference to the drawing accompanying the Provisional Specification.

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Chartered Patent Agent,

Agent for the Applicants.

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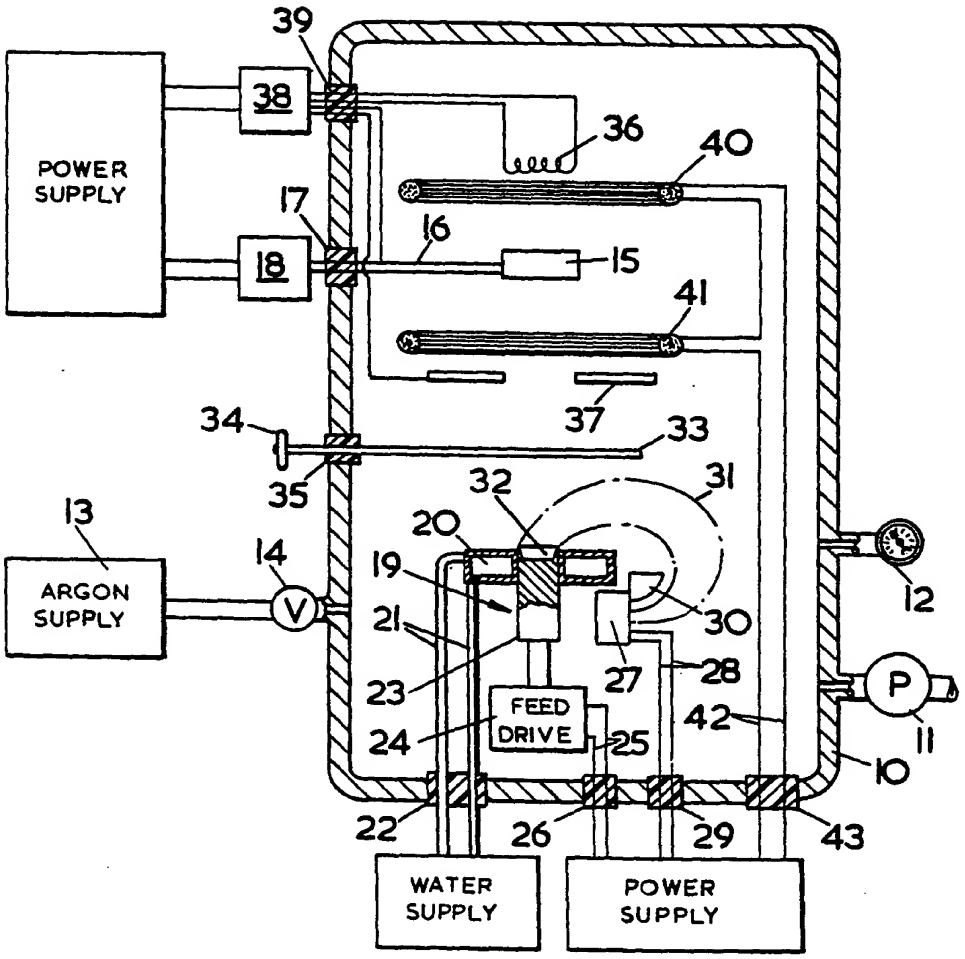
1 SHEET

PROVISIONAL SPECIFICATION

This drawing is a reproduction of the Original on a reduced scale.



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